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71 Applicant: Cordis Corporation  
14201 N.W. 60th Avenue  
Miami Lakes Florida 33014(US)

72 Inventor: Trotta, Thomas  
11920, N.E. 11th Place  
Miami, Florida 33161(US)

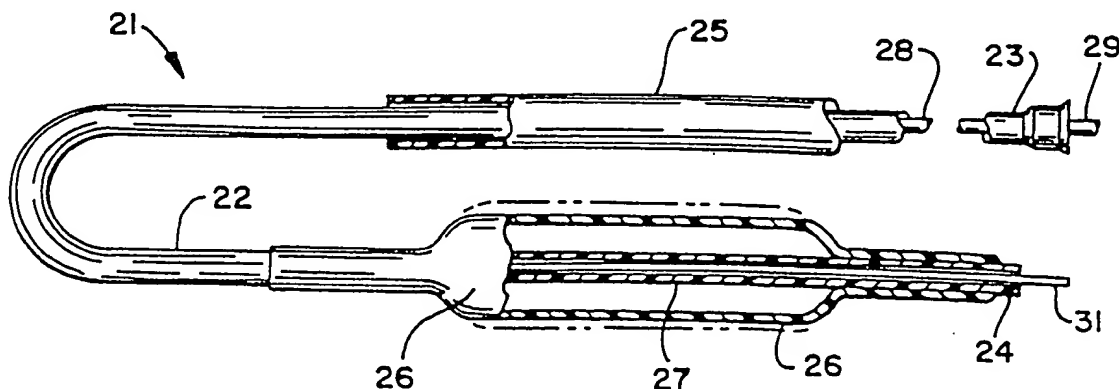
74 Representative: KUHNEN, WACKER &  
PARTNER  
Patent- und Rechtsanwaltsbüro,  
Alois-Steineckerstrasse 22  
D-85354 Freising (DE)

DOC

54 Polyetheramide tubing for medical devices.

57 Medical device tubing is prepared from a blend of polyetheramide having substantially no ester linkages with either or both a polyamide and a polyesteretheramide. The resulting tubing has an exceptionally high burst strength to flexibility ratio, and migration of monomers to the surface resulting in blooming is substantially retarded.

FIG. 1



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*// (A 61L 29/00 E 8, 108 L 97/19, 97/00)*

possible to blend these materials to provide a more flexible or softer extruded polymer that is more suitable for a tip portion of a catheter, while a different blend is less flexible and provides an extruded tubing that is more suitable for a catheter body requiring good torque control.

It has been found, however, that many of these polymers do not provide adequate burst strength properties and especially do not afford an extremely high burst strength to flexibility ratio which can be important for especially difficult medical device tubing applications. Another shortcoming of polymers or polymer blends such as the PEBA polyether block amide or ester-linked polyether-polyamide copolymers is the development of undesirable blooming which develops in much of this tubing after it has been stored for lengths of time that can be experienced during the normal commercial channels through which medical devices pass. Accordingly, at times when a medical professional removes a catheter or the like from its sterilized packaging, a quite noticeable quantity of blooming can be evident on the surface of the catheter, which can significantly reduce the confidence level that the medical professional has in the catheter. This has the potential of being detrimental to the supplier of the catheter and may result in loss of current and/or future sales.

It is currently believed that this blooming phenomenon is a manifestation of migration of monomers to the surface of the polymeric tubing. A fine white powder forms on the surface of the tubing as it ages at room temperature or after it has been subjected to heat treatment. This surface powder formation has the potential of adding to the foreign matter which enters the bloodstream or the like when the medical tubing contacts or otherwise communicates with the bloodstream or other portion of the body. Whether or not this represents a possible medical detriment, it nevertheless creates a perception of a product that is less than perfect. This is, of course, something to be avoided by suppliers of medical devices. For at least that reason alone, blooming is a phenomenon that is undesirable, and its avoidance can substantially increase the usefulness and value of the medical device.

Blooming can be detrimental for another reason. It is often desirable to provide a catheter or the like with a coating that is designed to impart lubricity or enhanced biocompatibility to the catheter, or to provide a means for administering a drug or the like. Blooming can interfere with these types of coatings, interfering with their adherence to the entirety of the catheter.

The present invention provides medical device components, particularly tubing for catheters and the like. The components are made from a polyetheramide material which can be extruded into a desired medical device component. The polyetheramide is a polyamide elastomer having substantially no ester linkages. It is preferred that the polyetheramide be blended with at least one other material falling within the general category of polyamide structures. Included in the grouping of other materials are polymers having polyamide structures per se as well as certain polyesteretheramides, especially those having a particularly high hardness such as Shore 70D or harder. When extruded, for example into tubing, the result is a material that has an extremely high burst strength to flexibility ratio and that retards blooming.

It is accordingly a general object of the present invention to provide improved medical device components, particularly tubing for catheters and the like.

Another object of the present invention is to provide an improved material and method for extruding medical device tubing.

Another object of this invention is to provide improved medical device tubing which incorporates polyetheramide materials that do not have any substantial ester linkages present within the polyetheramide.

Another object of the present invention is to provide improved polyetheramide or polyetheramide composition that exhibits an extremely high burst strength to flexibility ratio when extruded into medical device tubing.

Another object of this invention is to provide an improved polyamide-like or polyamide composition that retards blooming or the migration of monomers to the surface of tubing or the like which is extruded from the material.

These and other objects, features and advantages of the invention will be clearly understood through a consideration of the following detailed description.

#### Brief Description of the Drawings

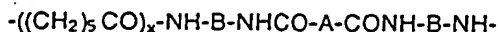
Fig. 1 is an elevational illustration, partially in cross section, of a catheter having a structure typical of one suitable for angioplasty;

Fig. 2 is a perspective view, partially broken away, of a catheter having a structure typical of a guiding catheter or the like;

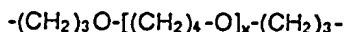
Fig. 3 is an elevational view, partially broken away, of a catheter having a structure typical of one suitable for use as an angiography catheter; and

designations are Grilamid ELY 60, which is especially preferred, and Grilon ELX 23 NZ.

Polyetheramides typically are prepared by directly reacting an amine-terminated soft segment with a dimer acid and caprolactam. As an example in this regard, when the amine-terminated soft segment is bis-(3-aminopropyl)-polyoxytetramethyleneglycol, and when the dimer acid is an acid such as EMPOL 1010, a PEA or PETA polymer of the following structure is formed:



wherein A designates dimer acid segments, B designates

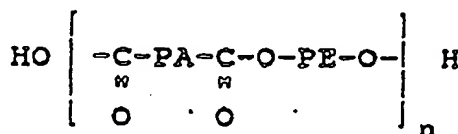


and x is an integer greater than 1. It will be noted that these formulas contain no ester linkages.

When it is desired to blend this polyetheramide material with the other polyamide-types of materials discussed herein, this polyetheramide having substantially no ester linkages will be present at between about 10 and about 90 percent by weight, based upon the total weight of the polymer blend. Typically any such blend will include between about 10 and about 90 percent by weight, based upon the total weight of the polymer blend, of a flexibility modifying polyamide type of material.

With more particular reference to the flexibility modifying polyamide-types of material, they can typically fall into two different categories, one being a polyamide per se, and the other being a polyesteretheramide, both of which have been found to decrease the flexibility of the polyetheramide. In the case of the polyesteretheramides, it is especially preferred that same exhibit a shore hardness of 70D or harder. Polyamides include the nylons such as Nylon 6, Nylon 11, Nylon 12 and the like as well as materials such as Grilamid L25. The general structure of these types of polyamides is, of course, quite well known, the structure having recurring polyamide groups (-CONH-) as an integral part of the polymer chain. The typical polyamide is a high molecular weight polymer in which these amide linkages occur along the molecular chain.

Polyesteretheramides, unlike the polyetheramides of the present invention, typically do have ester linkages. It is thought that this ester linkage contributes significantly to the blooming phenomenon which is generally exhibited by these types of polyesteretheramide materials. Included are the PEBA materials, namely the polyether block amide or ester-linked polyether-polyamide copolymer materials, which are believed to have a structure as follows:



wherein PA is a polyamide, PE is a polyether, and n is an integer greater than 1 which represents the number of blocks of copolymer molecular units within the molecular formula of the copolymer. Representative polyesteretheramide materials include the Pebax polymers. It has been found that, when the Pebax polymers are utilized, the bloom retardation characteristic of this invention is accomplished when the shore hardness is equal to or harder than Shore 70D.

The polyetheramide having substantially no ester linkages can be blended with one or more of these additional polyamide-types of materials in order to thereby increase the stiffness of the polyetheramide. It has been found that this increased stiffness does not bring with it a detrimental reduction in the extremely high burst strength to flexibility ratio or the excellent blooming retardation which has been found to be experienced by polyetheramides that are extruded into medical device tubing components. However, at least the excellent bloom retardation property is not maintained when the polyetheramide having substantially no ester linkages is blended and extruded with a polyesteretheramide which has a shore hardness less than Shore 70D.

With further references to the aspect of the present invention wherein blooming or migration of monomers to the surface is retarded, this feature is particularly advantageous in those instances where a coating is applied, such as a hydrogel coating, to the extruded polymer tubing. It has been found that such blooming undermines coatings which are applied. Exemplary coating materials which have enhanced effectiveness in accordance with their combination with the other aspects of this invention include hydrogel

tubing in accordance with this Example. The data show exceptionally high burst pressure yield points and, when combined with the data of Fig. 4, illustrate in excellent burst pressure strength to flexibility ratio.

The tubing was subjected to accelerated aging testing by passing it through aging cycles as follows. Each aging cycle proceeded by subjecting the tubing to alternating humidity cycling, with one week at 60 °C and 90 percent relative humidity alternating with one week at 60 °C and 10 percent relative humidity. All ratios produced tubing with minimal or no particle generation, thereby exemplifying excellent retardation of bloom development.

### Example 3

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The procedure of Example 2 was followed, except this time the polyetheramide Grilamid ELY60 was blended with the polyesteretheramide Pebax 7033 having a hardness of Shore 70D. The result of the stiffness testing is reported in Fig. 6, and the yield point data are reported in Fig. 5 by the circular data points. In both cases, both the as extruded and as annealed data are reported. The data show exceptional high burst strength to flexibility ratios.

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Accelerated aging tests were conducted as described in Example 2. Fig. 7 reports data for a blend of 36 percent polyetheramide having no ester linkages and 64 percent polyesteretheramide having a hardness of Shore 70D. An average of five samples were taken, and the vertical bar illustrated for each type of sample represents two standard deviations. The tubing was annealed at 150 °C for 30 minutes, then preconditioned and sterilized three times. In addition, the tensile properties were determined for these samples which had been subjected to accelerated aging conditions, and these data are reported in the Table.

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Table

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Treatment	Ultimate Elongation (%)	Force at Break (psi)	Tensile Strength at Break (psi)
Control	356	5.2	10,900
3 cycles	366	5.4	10,900
6 cycles	350	4.9	9,200
9 cycles	376	5.2	9,700

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In the Fig. 7 data, the "control" samples were untreated, and the "sterilized" samples were subjected to three conventional sterilization cycles. In the Table, the "control" was subjected to three sterilization cycles. In Fig. 7 and in the Table, "3 cycles", "6 cycles" and "9 cycles" refer to the aging cycles as described in Example 2. The data show that, even after accelerated aging, the excellent burst pressure and yield point at break are maintained even after this extensive aging which simulated typical storage aging of up to approximately 48 months. This was carried out by 9 aging cycles which is equivalent to storage for approximately 48 months at a 24 °C temperature. Furthermore, visual examination did not reveal any blooming until the 9th aging cycle was reached, at which point a small amount of powdering was detected on the interior of the tubing.

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The polyetheramide and polyesteretheramide blended tubing described in this Example and that is of the type in respect of which the data of Fig. 7 and the Table are reported had a yield point to stiffness ratio of 0.10 at a stiffness value of 25 kpsi. Similar testing on Pebax 6333 (a polyesteretheramide having a hardness of Shore 63D) had a stiffness ratio of 0.08 at a stiffness of 25 kpsi.

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It will be understood that the embodiments of the present invention which have been described are merely illustrative of a few of the applications of the principles of the present invention. Numerous modifications may be made by those skilled in the art without departing from the true spirit and scope of the invention.

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### Claims

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1. A medical device including a tubing component, the tubing component having been extruded from a polymer blend comprising:
  - between about 10 and about 90 percent by weight, based on the total weight of the polymer blend, of a polyetheramide component having substantially no ester linkages, and
  - between about 10 and about 90 percent by weight, based upon the total weight of the polymer blend, of a polyamide-type component selected from the group consisting of a polyamide, a

17. The angiographic catheter according to claim 15, wherein said catheter has a body and a tip, and said tip is constructed of said component.
18. The angiographic catheter according to claim 15, wherein the polyetheramide is Grilamid ELY60, the polyamide is Grilamid L25, and the polyesteretheramide is Pebax 7033.
19. A balloon dilatation catheter incorporating a tubing component, the tubing component having been extruded from a polymer blend comprising:
  - between about 10 and about 90 percent by weight, based on the total weight of the polymer blend, of a polyetheramide component having substantially no ester linkages, and
  - between about 10 and about 90 percent by weight, based upon the total weight of the polymer blend, of a polyamide-type component selected from the group consisting of a polyamide, a polyesteretheramide having a hardness of Shore 70D or harder, and combinations thereof; and
  - whereby the tubing component has an extremely high burst strength to flexibility ratio, and whereby the polymer blend tubing component substantially retards blooming thereof.
20. The dilatation catheter according to claim 19, wherein said catheter has a body and a tip, and said tubing component is a component of the body.
21. The dilatation catheter according to claim 19, wherein said catheter has a body and a tip, and said tip is constructed of said component.
22. The dilatation catheter according to claim 19, wherein the polyetheramide is Grilamid ELY60, the polyamide is Grilamid L25, and the polyesteretheramide is Pebax 7033.
23. A method for retarding blooming in medical device tubing, comprising:
  - formulating a polymer blend having between about 10 and 90 percent by weight, based upon the total weight of the polymer blend, of a polyetheramide component having substantially no ester linkages and further having between about 10 and about 90 percent by weight, based upon the total weight of the polymer blend, of a polyamide-type component selected from the group consisting of a polyamide, a polyesteretheramide and combinations thereof;
  - extruding the polymer blend into a length of polymer tubing; and
  - storing the length of polymer tubing for up to about six months or more under ambient storage conditions without experiencing any substantial migration of monomers to the surface of the polymer tubing.
24. The method according to claim 23, further including coating the polymer tubing with a lubricous coating material.
25. The method according to claim 23, further including coating the polymer tubing with a hydrogel coating material.
26. The method according to claim 23, wherein said storing for up to about six months or more under ambient storage conditions is substantially equivalent to accelerated aging by subjecting the tubing to a plurality of aging cycles, each cycle being in an environment of 60 ° C. and 90% relative humidity for one week followed by an environment of 60 ° C. and 10% relative humidity for another week.

FIG. 1

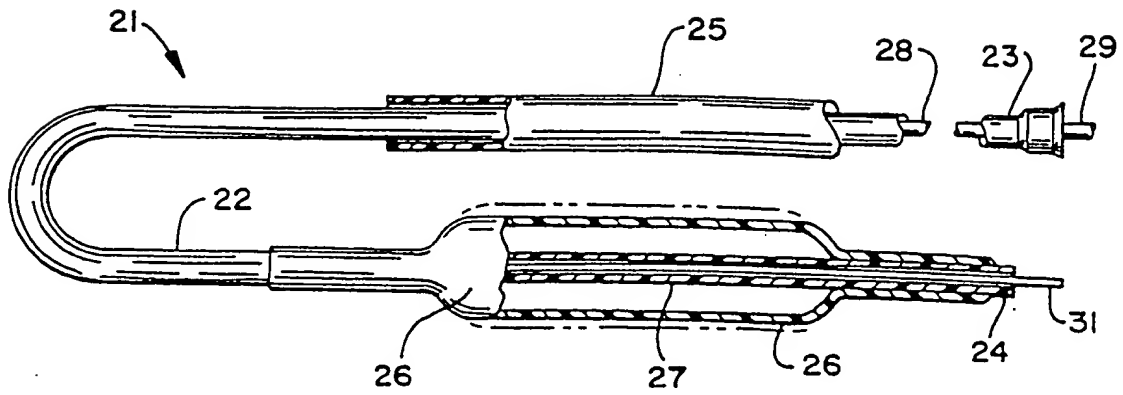


FIG. 2

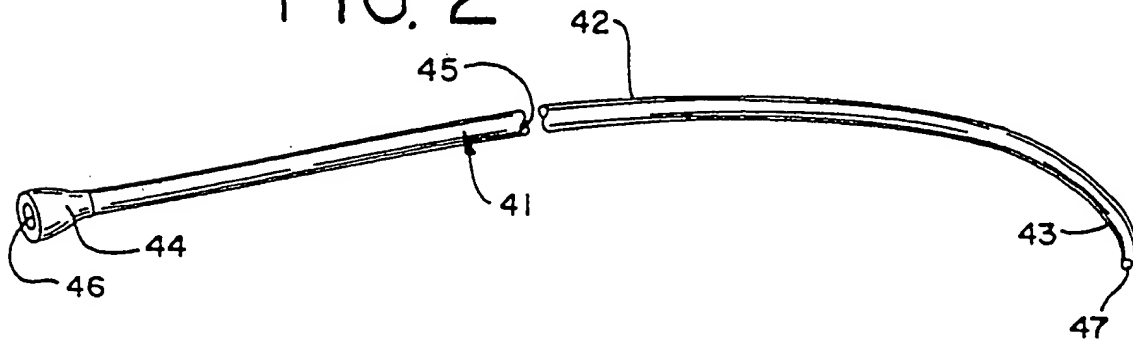
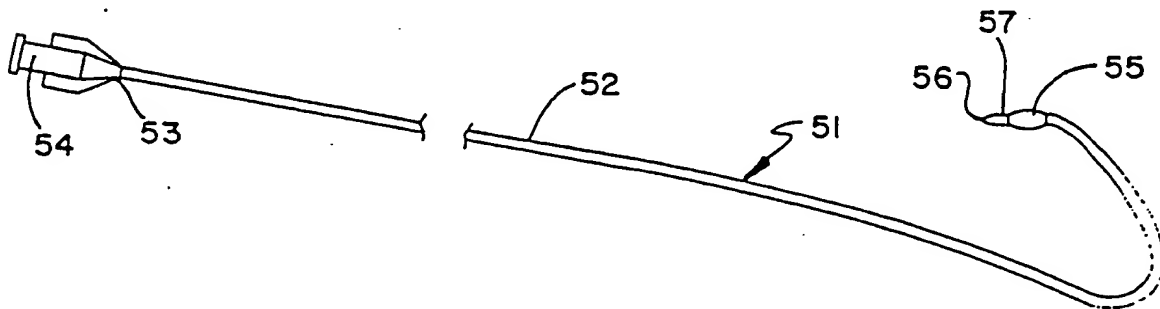
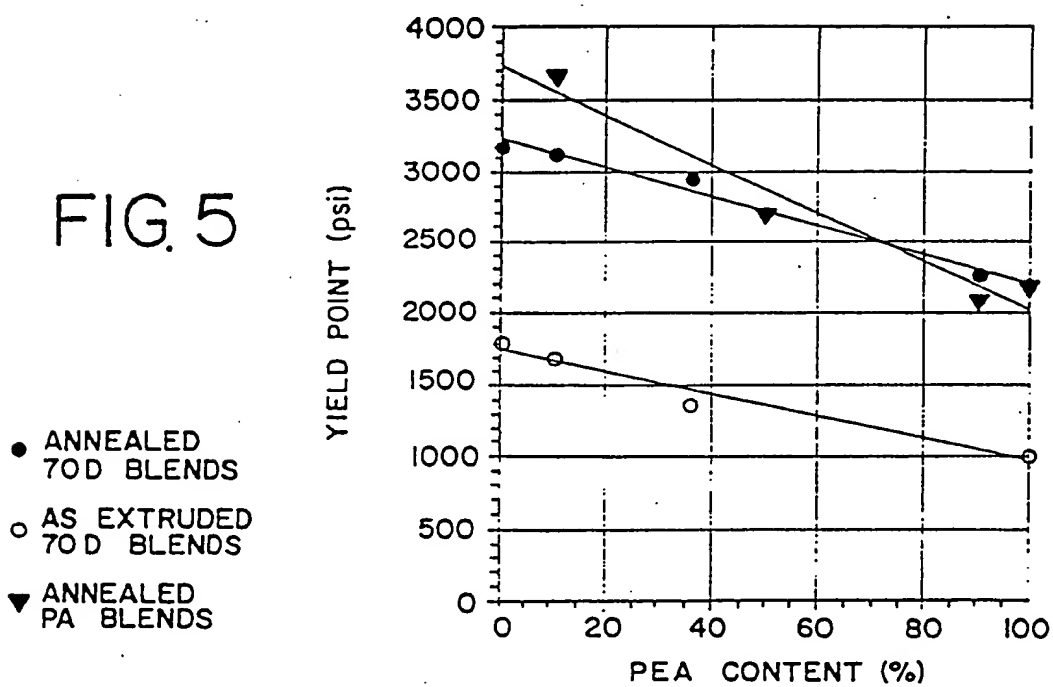
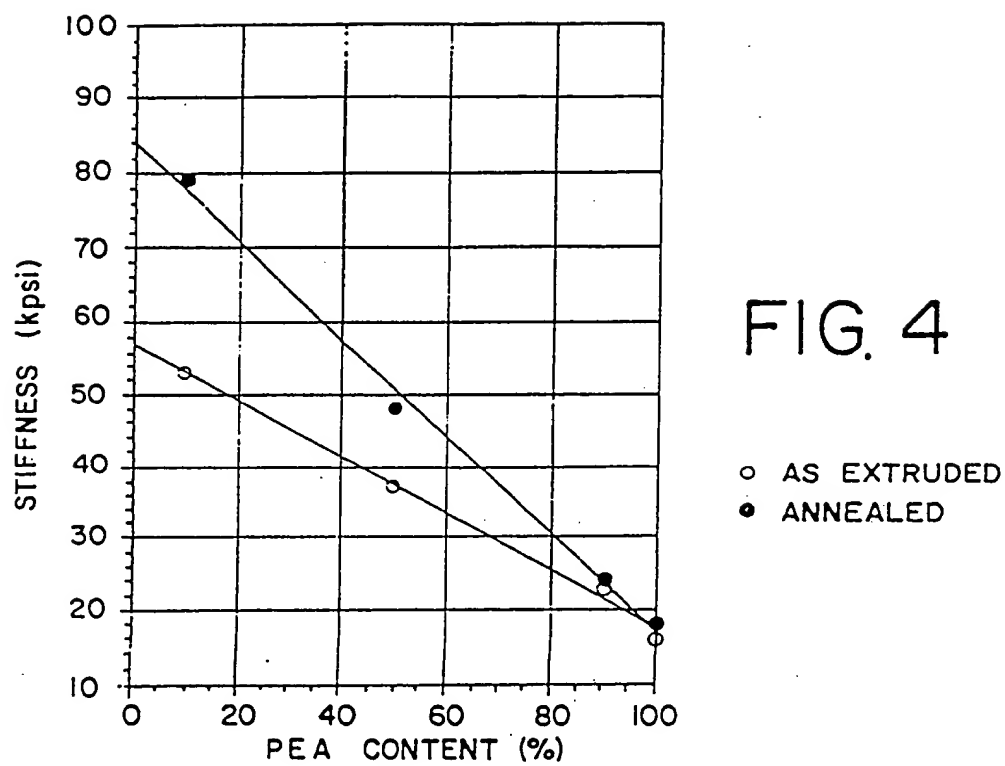
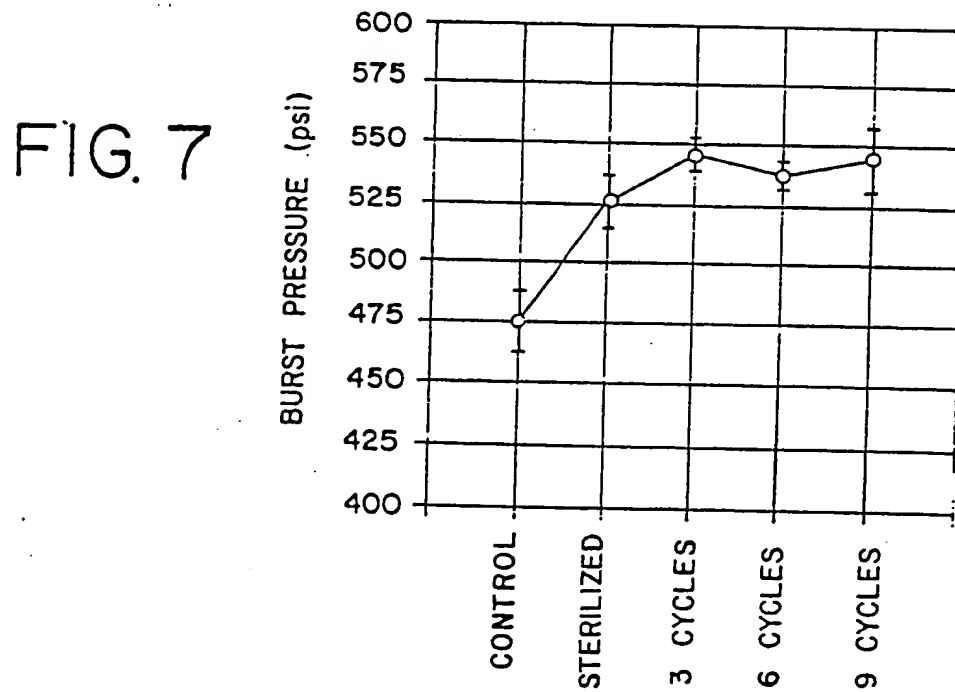
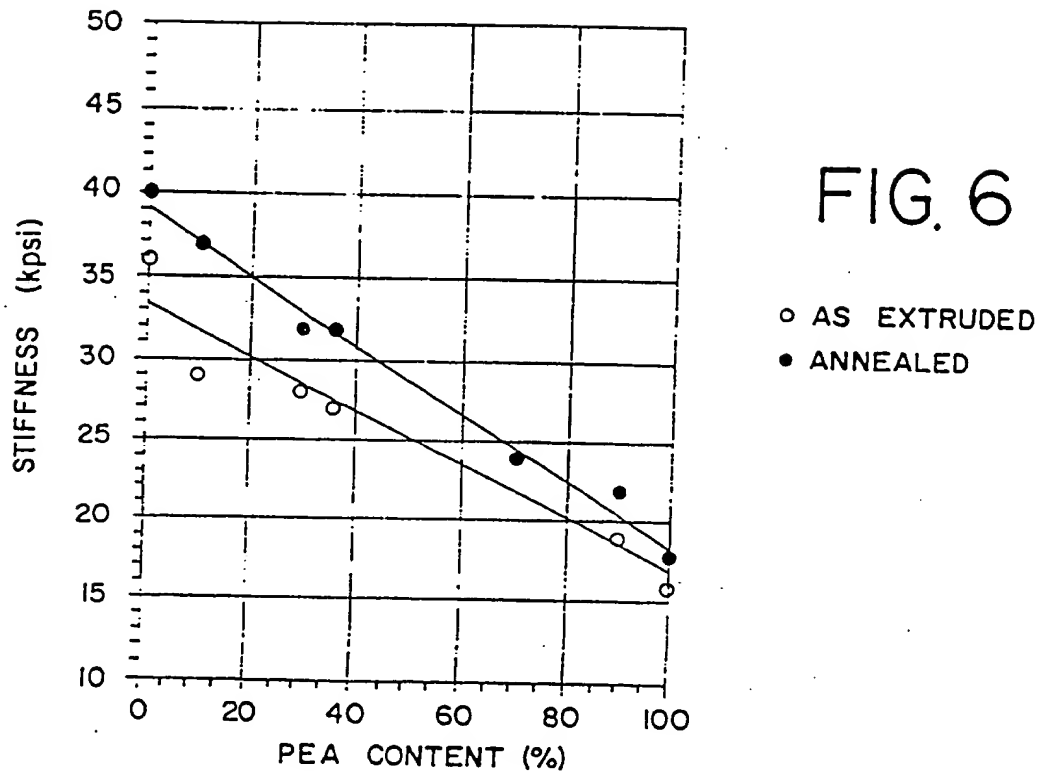


FIG. 3









European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 10 6805

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 651 681 (MEDICORP) * claim 1 *	1	A61L29/00
A	WO-A-8 401 513 (HARDCASTLE D.) * claim 4 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A61L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 NOVEMBER 1992	Examiner PELTRE CHR.
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